Scientific Bulletin. Series F. Biotechnologies, Vol. XVIII, 2014
ISSN 2285-1364, CD-ROM ISSN 2285-5521, ISSN Online 2285-1372, ISSN-L 2285-1364

BIOPOLYMERS BASED ON RENEWABLE RESOURCES - A REVIEW

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Abstract

It is well known that plastic waste has become a great problem for the environment all over the world. Conventional polymeric materials are not easily degraded because they are resistant against microbial attack; they accumulate in the environment and represent a significant source of environmental pollution. These problems caused by synthetic waste have led to the need for developing new polymeric materials that can be biodegradable and biocompatible with the environment, to replace the conventional ones. Over the past years a lot of attention has been paid to biodegradable polymers based on renewable resources because of their wide range of applications in packaging, agriculture or biomedical fields. This paper aims to present a review regarding the development of biopolymers and biocomposites based on renewable resources, their properties and the area of their application.

Key words: *biodegradable, biocomposites, biopolymers, renewable resources.*

INTRODUCTION

Materials made from synthetic polymers are not biodegradable and are often improperly discarded (Suchada C., 2010). The huge development of conventional plastics made from petroleum-based synthetic polymers unable to degrade in landfill or compost-like environment had led to serious environmental issues. In response to this increasing awareness, the use of polymers stemming from renewable and sustainable resources to develop biopolymers constitutes an innovative and promising alternative to reduce greenhouse gas and toxic emissions, reduce energy demand and the use of non-renewable resources (Godoia F.C. et al., 2011; Hassan M.A. et al., 2013; Payam M. et al., 2010; Chevillard A. et al., 2011).

Natural polymers derived from agricultural products (such as starch, proteins, cellulose and plant oils) are the major resource for developing renewable and biodegradable polymer materials to replace petrochemicals in many industrial applications due to increased environmental concern and diminishing petrochemical resources (Raquez J.M. et al., 2013; Xiaoqing Z. et al., 2010). Particularly, renewable agricultural and biomass feedstock have shown much promise for use in eco-efficient packaging to replace petroleum feedstock without competing with food crops (Abdelwahab M.A. et al., 2012). However, as compared to thermoplastic synthetic polymers, biopolymers present problems when processed with traditional technologies and show inferior performances in terms of functional and structural properties (Mensitieri G. et al., 2011).

In recent years, there has been an important increase in interest in the use of biodegradable materials for packaging, agriculture, medicine and other areas. A number of blends using biopolymers can be the alternative of currently used synthetic polymeric materials. The most common and potential biopolymers are starch, chitosan, alginate, gelatin, PLA, PHAs, etc. (Akter N. et al., 2012).

The term *biopolymer* is generally understood as an organic polymer that is produced naturally by living organisms (Armentano I. et al., 2013). One major advantage of biopolymers is that they are also fully capable of biodegradation at accelerated rates, breaking down cleanly into simple molecules found in the environment, such as carbon dioxide, water or methane, under the enzymatic action of microorganisms, in a defined period of time. Polymeric materials derived from renewable resources can be biodegradable or compostable under specific environmental conditions. They are classified according to the method of production or their source:

- Polymers directly extracted or removed from biomass such as polysaccharides and proteins.
- Polymers produced by classical chemical synthesis starting from renewable bio-based monomers such as polylactic acid (PLA).
- Polymers produced by microorganisms or genetically modified bacteria such as polyhydroxyalkanoates, bacterial cellulose, etc. (Mensitieri G. et al., 2011).

POLYSACCHARIDES AND PROTEINS

Starch is a potentially interesting biodegradable material due to its availability, low cost and renewability. Moreover, the use of starch in the plastics industry can reduce dependence on synthetic polymers. Although its structure has not been fully elucidated, it was established that starch is a heterogeneous material consisting primarily of two types of polymers: amylose (Figure 1) and amylopectin (Figure 2).

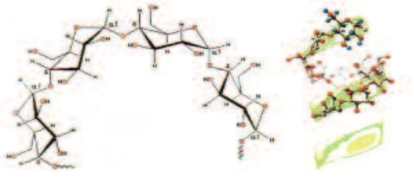


Figure 1. Chemical structure for amylase

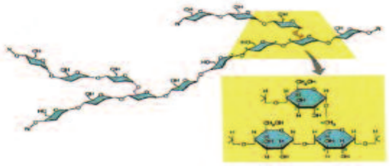
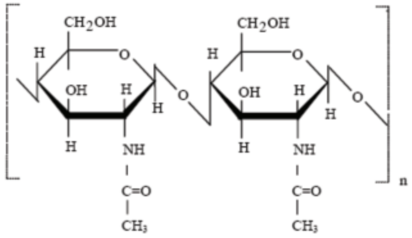


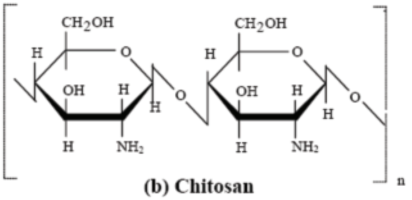
Figure 2. Chemical structure for amylopectin

Starch is a widely used material for making biodegradable plastics, but pure starch based films possesses low mechanical properties (Akter N. et al., 2012). Starch is the most important polysaccharide; it is the most abundant in nature and relatively inexpensive. Natural starch exists in granular form and, as such, it has been used as filler in polymers, but it can also be processed with classical plastic processing technologies such as extrusion, foaming and film blowing after thermoplasticization. The main limitation for starch is its hydrophilic nature, which limits its use in high moisture environments (Mensitieri G. et al., 2011). Starch can be successfully used in PLA composites (Qingfeng S. et al., 2011), and it can also be mixed with polyvinyl alcohol, poly-hydroxybutyric acid, polycaprolactone, chitosan, derivatives, and other degradable polymers to prepare fully degradable biomaterials (Wang Z. et al, 2008). Starch can be used as drug delivery carriers in tissue engineering applications (Thombre N. A. et al., 2009), membranes in direct contact with living tissues (Baran E.T. et al., 2004), microcellular foams (Manoi K. and Rizvi S.S.H., 2010) and food industry (Majzoobi M. et al., 2009; Omojola M. O. et al., 2012; Li B.Z. at al., 2009; Chung H.J. et al., 2008; Dang H.V. et al., 2008; Anand U. and Ambarish J., 2011).

Chitosan, as a unique positively charged polysaccharide, has been one of the most popular biopolymers for development of drug delivery systems for various applications, due to its promising properties, including high biocompatibility, excellent biodegradability, low toxicity, as well as abundant availability and low production cost (Bomou M. et al., 2014; Yangchao L. and Qin W., 2014). Chitosan is a biopolymer derived by deacetylation of chitin, which is the second most abundant biopolymer in nature after cellulose. Chemical structure of chitin and chitosan is shown in Figure 3.



(a) Chitin



(b) Chitosan

Figure 3. Chitin and chitosan structures

Chitin is present in the exoskeleton of arthropods such as insects, crabs, shrimps, lobsters and certain fungal cell walls. The production of chitosan from crustacean shells, wastes of the seafood industry, is economically feasible. Chitosan has been reported as a potential material of food packaging, especially as edible films and coatings due to its film forming properties. However, one of the main drawbacks of chitosan based materials relates to its relatively weak mechanical strength. Because of reactive amino and hydroxyl functional groups, chitosan is frequently blended with other polymers or crosslinked to improve their functional properties by inducing inter- or intra-molecular crosslinking in the polymer matrix (Yangchao L. and Qin W., 2014; Akter N. et al., 2012; Liang S. et al., 2009; Belalia et al., 2008; Vroman and Tighzert, 2009; Khwaldia et al., 2010; Agostino et al., 2012; Zuang et al., 2012).

The antibacterial activity of chitosan is affected by molecular weight and degree of deacetylation. Low molecular weight chitosan has strong antibacterial properties and it is also harmless to human body. For the food packaging industry, food quality and safety to human health are the two major concerns as consumers prefer fresh and minimally processed products. Chitosan has proven a useful antimicrobial agent in food processing, particularly for improving the shelf life of food materials (Bano I. et al., 2014; Jooyeoun J. and Yanyun Z., 2014; Sanches-Silva et al., 2010). Chitosan and its derivatives have been receiving significant scientific interests and became one of the hottest topics in recent decades, especially for its food, medical and pharmaceutical applications, including drug delivery and tissue engineering (Huang J. et al., 2012; Jooyeoun J. and Yanyun Z., 2014; Yangchao L. and Qin W., 2014; Lavorgna et al., 2014; Sweetie R., et al., 2012, Dash M. et al., 2011). Chitosan membrane, an important form of chitosan, presents potential application in tissue engineering, food preservation, wastewater purification, environmental protection, fuel cell and separation technology (Bomou M. et al., 2014).

Cellulose is a very important and fascinating biopolymer and an almost inexhaustible and sustainable natural polymeric raw material, which is of special importance both in industries and in daily lives (Weili H. et al., 2014). It is found in the cell walls of superior plants in the form of microfibrils with a helical organization on several levels containing crystalline domains (domains with ordering high cellulose chains) and amorphous (segment fields distorted, twisted and deformed) (Figure 4).

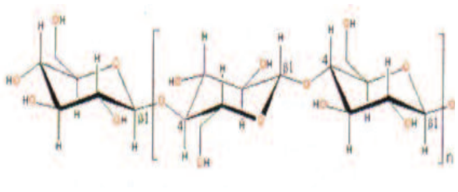


Figure 4. Chemical structure of cellulose

Cellulose is the most abundant biomass material in nature, and possesses some promising properties, such as mechanical robustness, hydrophilicity, biocompatibility, biodegradability, relative thermostability, high sorption capacity and alterable optical appearance (Weili H. et al., 2014; Xiaoyun Q. and Shuwen H., 2013). Cellulose has been widely applied in many fields. Biocomposites based on cellulose have great advantages (especially their intelligent behaviors in reaction to environmental stimuli) and they can be applied to many circumstances. Approximately 5×1011 metric tons of cellulose is being generated yearly. Unfortunately, only 2% is recovered industrially. The great properties of cellulose enable it to be applied to a vast array of fields (Xiaoyun Q. and Shuwen H., 2013).

Collagen has been extensively used as a biomaterial in many biomedical applications. Collagens are the most abundant proteins found in extracellular matrices of vertebrate animals (Vroman I. and Tighzert L., 2009). In animal hides and skins, the dominant collagen is type I and it is also the major structural component of tendon, bone and connective tissue. Collagen exists in the form of fibrils and they provide the main mechanical support and structural organization of connective tissues. Because collagens provide natural structure, biodegradability, and biocompatibility, they have extensive applications as a biomaterial in tissue engineering, wound healing, as drug carriers, and cosmetics. For example, fibril-forming collagens provide a scaffold for cell attachment and migration, as well as providing specific mechanical properties (Ganesh S. et al., 2014, Hoyer B. et al., 2014). Because of the presence of collagen, the animal derived tissues are used for the replacement of human tissues that results in the improvement of the wound-healing process. Furthermore, it has been used as the main component in the design of biomaterials such as artificial dermis, wound dressings, tissue engineering devices, tendon substitutes, and injectable material in plastic surgery. Collagen from animals, particularly from bovine species, is more advantageous due to the possibility of extraction of a large quantity of pure type I collagen. The structure and stability of collagen are thus an important factor as it is widely used as biomaterials (Ganesh S. et al., 2014).

The major challenge in the material research is to develop suitable modification methodologies to improve the properties of natural polymers. One example is the development of wheat proteins or wheat *gluten* - based natural polymer materials. As one of the cheapest plant proteins derived from the second largest cereal crop wheat (after maize), wheat proteins or wheat gluten have excellent properties in viscoelastic performance, tensile strength and gas barrier performance (Xiaoqing Z. et al., 2010). Wheat gluten, a by-product of the starch industry with a high protein content (>75 wt %), could be considered suitable for lots of applications because of its good thermoplastic properties, good processability and its remarkable biodegradability. Moreover, the use of protein as raw material offers a wide spectrum of chemical functionalities due to the large variety of amino acids, and also represents a significant source of nitrogen for the crops nutrition, a huge advantage for agricultural applications (Chevillard A. et al., 2011, 2012). Wheat gluten is mainly constituted of two main storage proteins that are gliadins (monomeric proteins with molecular weight ranging from 15 to 85 kDa) and glutenins (macro polymer with molecular weight ranging from 150 to more than 103 kDa). Gluten proteins can undergo disulphide interchange upon heating, which leads to the formation of a three-dimensional macromolecular network (Chevillard A. et al., 2011).

CHEMICAL SYNTHESIS PRODUCED POLYMER (PLA)

In the framework of environmentally friendly processes and products, polylactide (PLA) represents the best polymeric substitutes for various petropolymers because of its renewability, biodegradability, biocompatibility, good thermomechanical properties and relatively low cost (Armentano I. et al., 2013; Raquez J.M. et al., 2013). Chemical structure of PLA is shown in Figure 5.

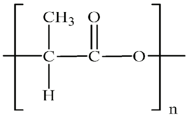


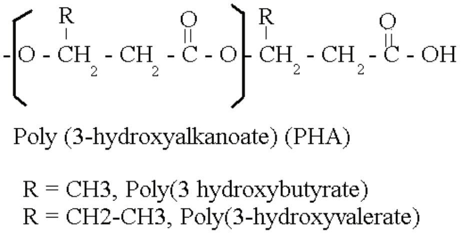
Figure 5. Chemical structure of PLA

Initially, most of its applications concerned biomedical sector and short time uses such as packaging, particularly for the biodegradable properties of PLA. Interestingly, due to the depletion of petroleum resources, PLA is now seen more and more as a valuable biosourced polymer alternative in long term applications such as automotive and electronics (Abdelwahab M.A. et al., 2012; Lasprilla A.J.R. et al., 2012; Raquez J.M. et al., 2013). PLA is an eco-friendly product with better features for use in the human body (nontoxicity). Lactic acid polymers can be synthesized by different processes so as to obtain products with an ample variety of chemical and mechanical properties. Due to their excellent biocompatibility and mechanical properties, PLA and its copolymers are becoming widely used in tissue engineering for function restoration of impaired tissues. It is a highly versatile biodegradable polymer, which can be tailored into different resin grades for processing into a wide spectrum of products. Polymers based on lactic acid (PLA) are a most promising category of polymers made from renewable resources (Lasprilla A.J.R. et al., 2012). PLA exhibits several advantages in relation to the petroleum-based polymers usually used for packaging (Armentano I. et al., 2013): (i) Good transparency, usually defined as the transmission of visible light in the range of 540–560 nm, slightly higher than that of poly(ethylene terephthalate) (PET) and poly(styrene) (PS); (ii) Degradation in biological environment such as soil or compost; (iii) Biocompatibility: PLA has been demonstrated to be biocompatible and to degrade into non-toxic components and it has been approved by the Food and Drug Administration (FDA) for implantation in the human body; (iv) Process ability: The main conversion approaches of PLA are based on melt processing.

Unfortunately, PLA is rigid and brittle at room temperature due to its glass transition temperature (Tg) close to about 55°C. PLA is a glassy polymer with poor elongation at break (typically less than 10%) (Xiao L. et al., 2012). To improve the ductility of PLA-based materials, a large number of investigations have been made to modify its properties via plasticization and blending with other polymers. However, a great number of variables, i.e. nature of PLA matrix, type, and optimal percentage of plasticizer, thermal stability at the processing temperature, etc. must be considered (Hassouna F. et al., 2011, Abdelwahab M.A. et al., 2012; Halasz K. and Csóka L., 2013). PLA is a linear aliphatic thermoplastic polyester derived from 100% renewable resources such as sugar, corn, potatoes, cane, beet, etc. (Armentano I. et al., 2013).

POLYMERS PRODUCED BY MICROORGANISMS

Polyesters are now universally used as fibers and films in various areas, while plastic waste management recently became a critical problem of global environment. *Polyhydroxyalkanoate* (PHA), which is produced from renewable carbon resources by many microorganisms, is an environmentally compatible polymeric material and can be processed into films and fibers. Also, findings suggest that PHA is a suitable material for fabrication of resorbable medical devices, such as sutures, meshes, implants, and tissue engineering scaffolds (Brigham C.J. and Sinskey A.J., 2012; Chen G.Q and Wu Q., 2005). A wide variety of bacteria can accumulate these polymers as a carbon and energy storage material under nutrient imbalanced condition such as nitrogen, phosphorous or oxygen limitation together with excess carbon. They can be composed of over 100 different monomers and they act as a carbon/energy store for more than 300 species of Gram-positive and Gram-negative bacteria as well as a wide range of archaea (Davis R. et al., 2013; Keiji N. et al., 2009; Laycock B. et al., 2014; Suchada C. et al., 2010). PHAs can be produced from renewable raw materials and are degraded naturally by microorganisms that enable carbon dioxide and organic compound recycling in the ecosystem, providing a buffer to climate change (Suchada C., 2010). Biodegradation of PHA material occurs due to the action of extracellular PHA depolymerase secreted from microorganisms in various natural environments (Davis R. et al., 2013; Keiji N. et al., 2009; Laycock B. et al., 2014). Currently, new research efforts are proceeding towards developing PHAs in transgenic plants (Reddi M.M.et al., 2013). Polyhydroxybutyrate (PHB) and poly(hydroxybutyrate-cohydroxyvalerate) (PHBV) are the most well-known polymers of the polyhydroxyalkanoates family. Chemical structure of the most representative PHA is shown in Figure 6.



$$-\left[O-\overset{R}{\overset{|}{CH_2}}-CH_2-\overset{O}{\overset{\|}{C}}-O\right]-\overset{R}{\overset{|}{CH_2}}-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

Figure 6. PHA structure

Polyhydroxybutyrate (PHB) is polyester from the PHA family and is accumulated by a wide variety of micro-organisms as an intracellular storage source of organic carbon and chemical energy (Bertini F. et al., 2012).

The properties of the PHBV co-polymer can be easily tailored by varying the valerate content.

PHB is biodegradable thermoplastic polyester that can be considered analogous to many conventional petroleum-derived plastics currently in use. Furthermore, it has some additional advantages such as being biocompatible and can be produced from a renewable raw material in a sustainable technology from economical to ecological point of view (Godoia F.C. et. al., 2011).

Bacterial cellulose (BC) is a fascinating and renewable natural nanomaterial characterized by favorable properties such as remarkable mechanical properties, porosity, water absorbency, mold ability, biodegradability and excellent biological affinity.

Intensive research and exploration in the past few decades on BC nanomaterials mainly focused on their biosynthetic process to achieve the low-cost preparation and application in medical, food, advanced acoustic diaphragms, and other fields (Weili H. et al., 2014, Zhang S. and Luo J., 2011). Bacterial cellulose has the same molecular formula as plant cellulose, but with unique and sophisticated three-dimensional porous network structures. The cellulose obtained from bacteria is known to have unique properties over plant cellulose such as: (i) Absence of lignin and hemicellulose, making it a highly pure source of cellulose, (ii) High degree of polymerization combined with crystallinity (60–70%), leading to high Young's modulus at room and elevated temperatures, (iii) Extremely high water-holding capacity, up to 100 times its self-weight; (iv) Excellent biodegradability and biological affinity (Vitta S. and Thiruvengadam V., 2012).

Various modification methods have been explored to open up possibilities for endowing BC with new functionalities. In the last few years, growing worldwide activity can be observed regarding extensive scientific investigation and increasing efforts for the practical use of the BC materials. There is an increasing annual publication activity on BC (also known as microbial cellulose or bacterial nanocellulose). In recent years, the investigation and utilization of BC in functional materials have been the focus of research, and a growing number of works have been included in this field. Functional BC-based nanomaterial's are especially an attractive topic because they enable the creation of materials with improved or new properties by mixing multiple constituents and exploiting synergistic effects, such as electronic, optical, magnetic, catalytic properties and bioactivity (Weili H. et al., 2014, Castro C. et al., 2012).

CONCLUSIONS

Biodegradable natural polymers are mainly based on renewable resources (like starch, collagen, cellulose, etc.) and can be produced naturally or synthesized from renewable resources. Starch, collagen, chitosan, wheat gluten have all applications in agriculture, food industry, medicine, cosmetics, etc. PLA also has applications in many areas such as packaging industry and biomedical sector. Biobased and biodegradable polyesters like PHAs have been in demand in order to reduce carbon dioxide emissions from plastic waste and to build a sustainable society.

In view of expanding the scope of BC applications, it is important to take full advantage of the unique structure and properties of BC nanomaterials to develop novel BC-based nanomaterials with groundbreaking new features.

ACKNOWLEDGMENTS

This paper was *published under the frame of* European Social Fund, *Human Resources Development Operational Programme 2007-2013, project no.* POSDRU/159/1.5/S/132765.

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